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GAS ADSORPTION BY ACTIVATED AND IMPREGNATED CARBONS

QUARTERLY PROGRESS REPORT

April 1977 to July 1977

by

P. J. Reucroft
G. B. Freeman

October 1977

UNIVERSITY OF KENTUCKY
Lexington, Kentucky 40506
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HCN/H_2O mixed vapor isotherms were measured on BPL activated and ASC whetlerite carbons maintaining an essentially constant relative water pressure and varying the relative HCN pressure. Chemisorption data on ASC whetlerite showed water vapor retention varying randomly between 0.001 gm/gm and 0.012 gm/gm and HCN/H_2O retention decreasing from 0.050 gm/gm to 0.025 gm/gm with increasing HCN pressure.

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PREFACE

The work described in this report was authorized under Contract No. DAAA-15-74-C-0163, Task 1W762710A09501, Gas Adsorption by Activated and Impregnated Carbons. The work described covers the period from 9 April 1977 to 8 July 1977.

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GAS ADSORPTION BY ACTIVATED AND IMPREGNATED CARBONS

Quarterly Progress Report, April, 1977 to July, 1977

I. INTRODUCTION

The studies on mixed vapor adsorption by BPL activated and ASC whetlerite impregnated carbons reported in the last two reports have been continued.[1] A second set of data dealing with HCN/H_2O adsorption by BPL activated carbon has been compiled with the H_2O in the system kept constant, and is shown in Figure 1. The isotherm compiled from this data reveals more structure than the previous isotherm.[1b] A similar experimental technique was utilized to construct an HCN/H_2O adsorption isotherm on ASC whetlerite impregnated carbon keeping the H_2O relative pressure in the system between 0.8 and 0.9. The experimental method used with the ASC whetlerite impregnated carbon allowed acquisition of chemisorption data involving the retention of H_2O alone and of HCN/H_2O mixtures. These data are reported herein.

II. ADSORPTION OF HCN/H_2O MIXTURES BY BPL ACTIVATED AND ASC WHETLERITE IMPREGNATED CARBONS

The experimental procedure involving the adsorption of HCN/H_2O mixtures by BPL activated carbon is the same as that reported earlier[1b] and can be summarized as follows:

1. The BPL carbon was exposed to H_2O at a relative vapor pressure of 0.79 resulting in an adsorption of 0.358 gm/gm.
2. The H_2O was desorbed at 400°C and as much of that vapor retained in the storage flask as possible.
3. A suitable amount of HCN was added to the H_2O and the vapors were allowed to mix.
4. The BPL sample was re-exposed to the mixture.
5. This mixture was then desorbed at 400°C and the process continued with the addition of more HCN.

The chemisorbed component of H_2O, HCN, or HCN/H_2O was always less than 0.004 gm/gm throughout the entire course of the isotherm.

Previous work showed that HCN is chemisorbed by ASC whetlerite[2] to an extent that the previously described experimental procedure would

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[1a] P. J. Reucroft and G. B. Freeman, Eleventh Quarterly Report, October 1975 to January 1976, Edgewood Arsenal Contract DAAA15-74-C-0163.

[1b] P. J. Reucroft and G. B. Freeman, Twelfth Quarterly Report, January 1977 to April 1977, Edgewood Arsenal Contract DAAA15-74-C-0163.

[2] P. J. Reucroft and C. T. Chiou, Seventh Quarterly Report, October 1975 to January 1976, Edgewood Arsenal Contract DAAA15-74-C-0163.

not be feasible. Thus, the following procedure was employed and a fresh ASC whetlerite carbon sample was used for each data point:

1. The ASC whetlerite carbon was exposed to H_2O at a relative vapor pressure of between 0.8 and 0.9.

2. The H_2O was desorbed at 150°C and as much as possible retained in the storage flask.

3. A suitable amount of HCN was added to the H_2O and the vapors were allowed to mix.

4. The carbon was re-exposed to the mixture.

5. The mixture was desorbed at 150°C and the final mass of the carbon sample recorded.

The procedure described in the previous paragraph permitted the measurement of the H_2O retained as well as the HCN/H_2O mixture chemisorbed for each carbon sample examined. This allowed evaluation of the H_2O chemisorption and the HCN/H_2O chemisorption by a number of ASC whetlerite samples.

III. RESULTS AND DISCUSSION

Two distinct adsorption sites were postulated by Dubinin et al[3] to account for the small initial H_2O adsorption followed by the rapid rise. Initially, surface oxides in the micropores act as adsorption centers and permit adsorption by the formation of hydrogen bonds between the water molecules and the surface oxides. The secondary adsorption sites are the adsorbed water molecules which can retain other water molecules by means of hydrogen bonds. As the number of secondary adsorption sites increases, the rapid adsorption increase between $P/P_o = 0.4$ and 0.6 is due to the increasing probability of adsorption followed by eventual coalescence of these complexes. The hysteresis is due in part to the capillary condensation resulting from the action of the surface tension at the curved meniscus and in part due to the multimolecular adsorption.

The results of the mixed vapor isotherm may be analyzed in terms of the two types of primary adsorption sites on BPL activated carbon; carbon sites and surface oxides. It is possible to consistently describe each of the mixed vapor results by postulating that the HCN shows a greater affinity for the surface oxides and for the carbon sites than does the H_2O. The low affinity of the carbon sites for H_2O molecules would predict the additional adsorption of HCN by carbons in equilibrium with H_2O vapor. If, however, the carbon was pre-exposed to HCN, then the occupation of both the surface oxides and carbon sites would preclude the additional adsorption of any significant amounts of water. There is no short term evidence that the H_2O molecules will replace the

---

[3a] M. M. Dubinin, E. D. Zaverina, and V. V. Serpinsky, J. Chem. Soc., 1760 (1950).

adsorbed HCN molecules on the surface oxides. In the case of simultaneous adsorption of H_2O and HCN, some of the HCN is expected to be preferentially (with respect to the H_2O molecules) adsorbed on the surface oxides thereby robbing the H_2O of primary sites, and also precluding the formation on those sites of secondary adsorption sites. This predicts that, for high H_2O vapor levels, the small injection of HCN into a reservoir of H_2O, followed by the exposure of a BPL activated carbon to that mixture, would result in a smaller total adsorption than would the exposure of the BPL sample to the pure H_2O.

The ASC whetlerite composition differs from BPL activated carbon by the presence of impregnates. The results of the mixed vapor study on ASC whetlerite are qualitatively the same as those obtained on BPL activated carbon except in two respects. First, with the mixed vapor adsorption isotherm on ASC whetlerite, there is an initial rise in the amount adsorbed followed by the same behavior exhibited by the BPL carbon. This result is shown in Figure 2. Figure 2 is a graph of the difference between the amount of H_2O adsorbed and the amount of HCN/H_2O adsorbed by the carbon sample as a function of HCN relative pressure and shows results obtained for two BPL samples and one ASC whetlerite sample. Second, much more adsorbate is chemisorbed on the ASC whetlerite carbon in comparison with the BPL activated carbon. Both of these differences must be due to the influence of the impregnates. From Figure 3, it can be seen that the chemisorption of both HCN and H_2O is greater than the chemisorption of either of these adsorbates by BPL activated carbon. Thus, one or more of the impregnates shows a very strong affinity for H_2O and/or HCN. At low relative partial pressures (~0.001) of HCN in the mixed vapor isotherm for ASC whetlerite, the rise in adsorption might be interpreted by assuming that the HCN is preferentially adsorbed at an impregnate site. Until these sites are filled, the HCN does not interfere with the adsorption of the H_2O.

Figure 3 shows the chemisorption of H_2O, the chemisorption of the HCN/H_2O mixture and the difference between the two on ASC whetlerite carbon. Within the graph, successive points are arranged in order of increasing relative pressure of HCN. It is clear that the chemisorption of H_2O varies apparently randomly between about 0.001 gm/gm to about 0.012 gm/gm. The chemisorption of the HCN/H_2O mixture tends to decrease as a function of increasing HCN. The difference between the two chemisorptions was taken in an attempt to identify the increase in chemisorption due to simple chemisorption of HCN unrelated to the presence of H_2O in the system. Earlier data[2] gave chemisorption "saturation" values of about 0.031 gm/gm. at HCN relative pressures greater than 0.015 on ASC whetlerite. This value of HCN chemisorption generally compares favorably with the presently determined $W_{(HCN/H_2O)}-W_{H_2O}$ values in magnitude. The fluctuations observed are most likely due to the presence of the H_2O vapor.

[3b] M. M. Dubinin in Chemistry and Physics of Carbon, (P. L. Walker, Jr., ed.) Vol. 2, p. 111, Marcel Dekker Inc., New York 1966.

These explanations of the various processes described herein could be further clarified by 1) the presence of a gas analyzer on the system and 2) the measurement of pertinent thermodynamic quantities. The gas analyzer system would allow determination of the relative proportions of the vapors being adsorbed and the replacement of one adsorbate by another as a function of time. By measuring heats of adsorption it may be possible to identify the absorption affinities of the different sites for H_2O and/or HCN.

APPENDIX A

TABLES

TABLE 1. MIXED VAPOR ADSORPTION BY BPL ACTIVATED CARBON

P_{H_2O}/P_o	W_{H_2O}†	P_{HCN}/P_o	W_{HCN/H_2O}†
0.79	0.358	0.010	0.245
		0.015	0.236
		0.030	0.147
		0.040	0.145
		0.047	0.159
		0.064	0.176
		0.097	0.201

† gm of adsorbate/gm of adsorbent

TABLE 2. MIXED VAPOR ADSORPTION BY ASC WHETLERITE IMPREGNATED CARBON

Sample No.	P_{H_2O}/P_o	W_{H_2O}†	P_{HCN}/P_o	W_{HCN/H_2O}†	$W_{HCN/H_2O}-W_{H_2O}$
1	0.84	0.347	0.00125	0.372	0.025
4	0.89	0.369	0.0042	0.280	-0.089
5	0.87	0.379	0.0113	0.228	-0.151
6	0.85	0.344	0.0227	0.191	-0.153
7	0.87	0.353	0.0322	0.179	-0.174
8	0.85	0.340	0.0514	0.155	-0.185
9	0.93	0.372	0.0693	0.212	-0.160

† gm of adsorbate/gm of adsorbent

APPENDIX A

TABLE 3. CHEMISORPTION DATA ON ASC WHETLERITE IMPREGNATED CARBON

W (gm of adsorbate/gm adsorbent)

Sample No.	W_{H_2O}	$W_{(HCN/H_2)}$	$W_{(HCN/H_2O)}-W_{H_2O}$
1	0.0115	0.050	0.039
2	0.0045	0.049	0.045
3	0.0010	0.047	0.046
4	0.0042	0.030	0.026
5	0.0053	0.032	0.027
6	0.0099	0.032	0.022
7	0.0087	0.030	0.021
8	0.0012	0.028	0.029
9	0.0025	0.025	0.022

APPENDIX A

APPENDIX B

Figures

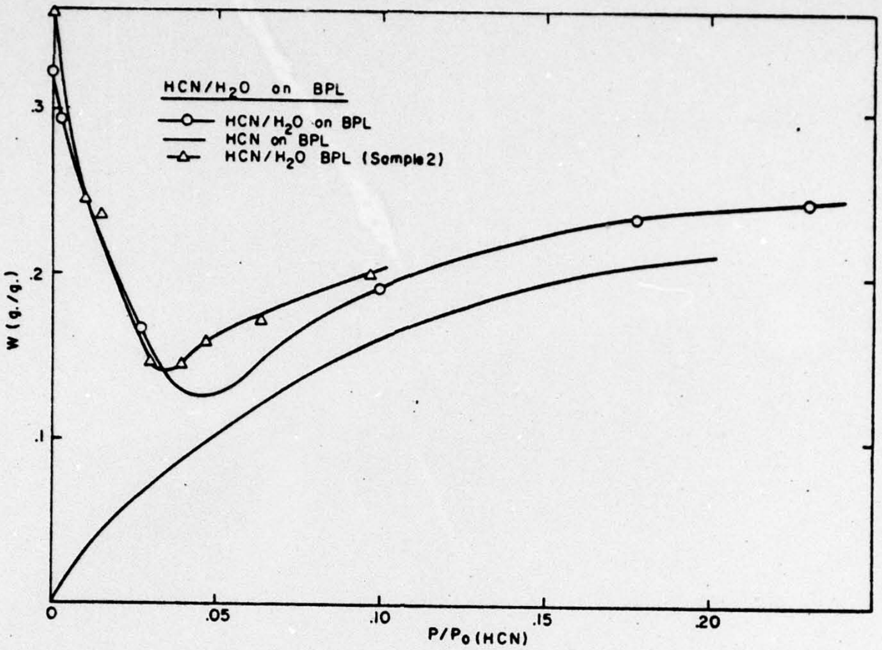

Figure 1. Adsorption of HCN/H_2O Mixtures by BPL Activated Carbon

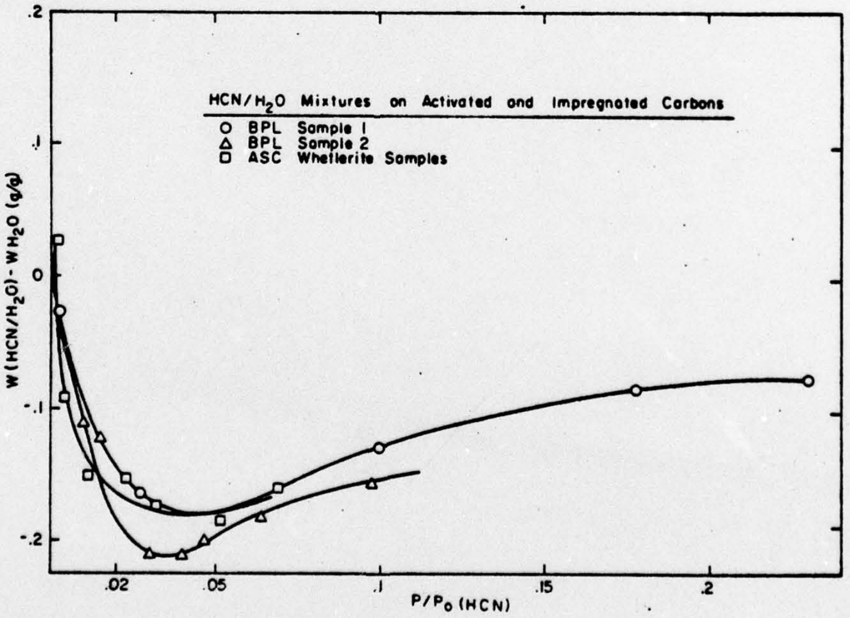

Figure 2. Adsorption of HCN/H_2O Mixtures by BPL Activated and ASC Whetlerite Carbons

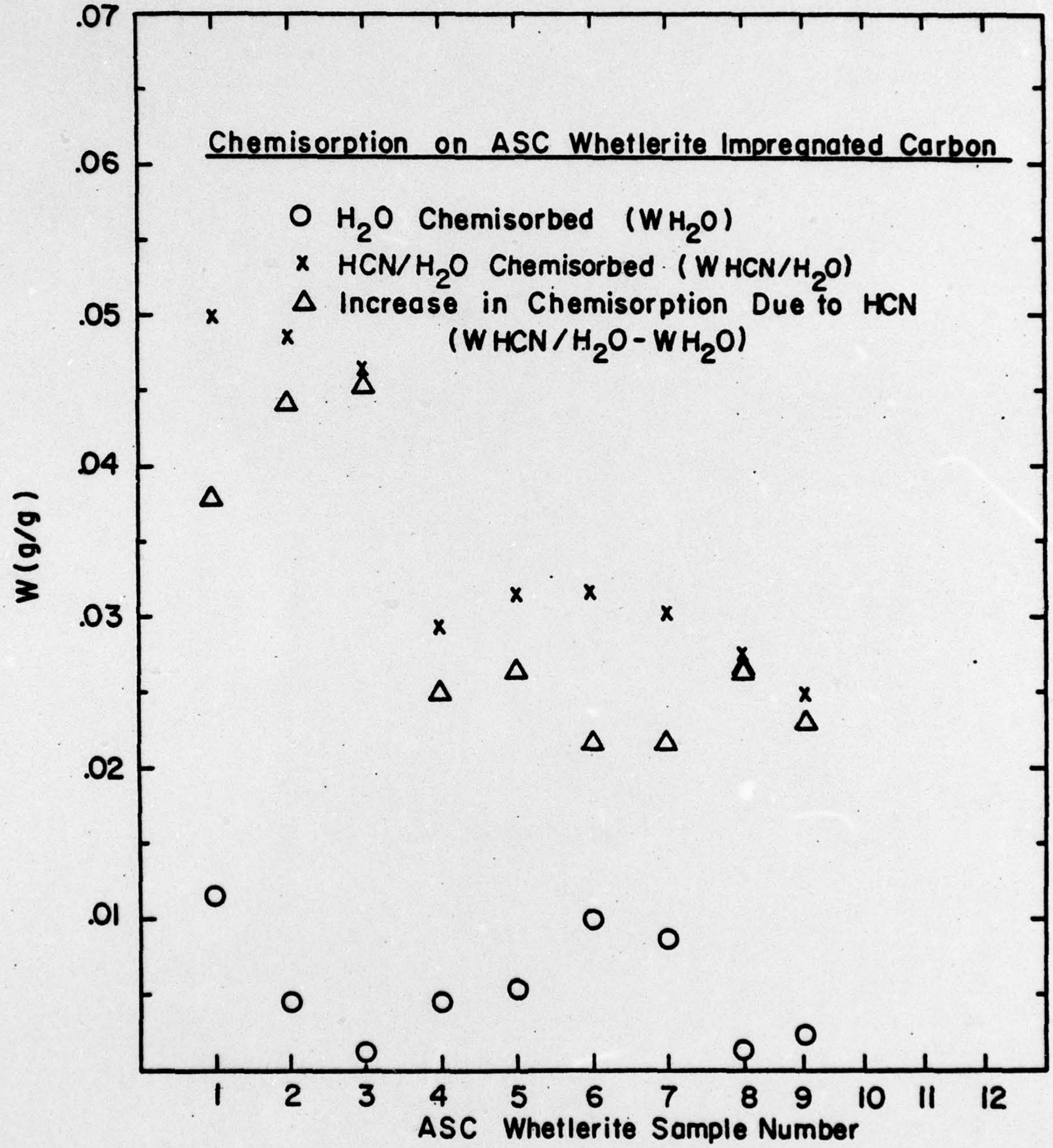

Figure 3. Chemisorption by ASC Whetlerite Impregnated Carbons

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